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FIRST BIMONTHLY PROGRESS REPORT

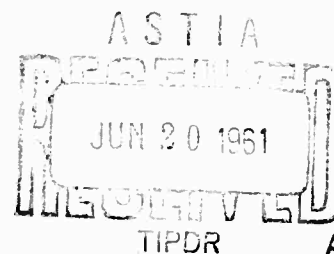
Covering the Period

1 April 1961 to 31 May 1961

TITLE: ACCELERATED DETERIORATION  
OF TEXTILES

Prepared by

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## INTRODUCTION

The textile deterioration program encompasses studies on the accelerated degradation of the various important textile fibers encountered in military apparel and material. Although other degradative chemical reactions may be visualized, the two now considered most important are catalyzed atmospheric oxidation and catalyzed hydrolysis by atmospheric moisture. All combinations of deteriorating chemical reactions and fibers to be deteriorated are being explored. One of the most promising of these is the photocatalyzed atmospheric oxidation of cellulose.

During previous work under contract Onl-136 it was found that several different metallic ions, in the presence of actinic light, can catalyze the photochemical oxidative degradation of cellulose. Ferric and ceric ions were found to be especially effective.

Work during the present report period has been devoted entirely to studying the photooxidative degradation of cellulose, catalyzed by ferric ion.

## SUMMARY

The object of these studies was to measure, quantitatively, the photocatalytic effect of ferric ion on the oxidative degradation of cellulose. Cellophane was chosen as the substrate, rather than the woven cellulosic fabrics used previously, for the following reasons: (1) With cellophane it is possible to measure accurately the amount of catalyst needed to cause a given degree of degradation. Even deposition of catalyst can be achieved in cellophane, but is practically impossible to attain in the woven fabrics. (2) The simpler structure of cellophane enables accurate measurement of the amount of light needed to cause degradation. Practically all of the light falling on the cellophane is absorbed, reflected specularly, or transmitted, with very little scattering. A large proportion of the light falling on a

woven fabric is scattered, making measurement difficult. (3) The simple structure of cellophane facilitates accurate measurement of physical properties such as tensile strength. The cellophane sheets have uniform thickness, while in a woven fabric the yarn and fiber sizes, as well as thread counts, are variable.

In the initial experiments herein reported, cellophane sheets, uniformly impregnated with ferric nitrate to a ferric ion content of 0.1%, were used as the test material. Three sheets were set up in tandem and this assembly was exposed to filtered carbon arc radiation comprising wave lengths of 3600 to 7000 A. Untreated cellophane was used as the control. The deterioration of the cellophane was determined by tensile strength measurements. The limited results obtained to date indicate that a five hour exposure, under these conditions, affected neither the treated sheets nor the untreated sheets to an appreciable extent.

Photometric measurements showed that the light transmittance of the untreated cellophane was 88% at 3600 A, compared to a transmittance of 70% for the treated cellophane. At 4000 A, the transmittances of untreated and treated cellophane were 89% and 81%, respectively. Both transmitted about 90% at wave lengths over 4500 A, up to 7000 A. Thus, in the three-sheet tandem arrangements, the second sheet received less light than the first, and the third sheet received corresponding much less light.

Since it has been shown previously (Final Summary Report on Contract Cml-136, dated 28 February 1961) that as little as 0.004% ferric ion in a cotton fabric can accelerate photooxidative degradation of the cotton, it is expected that longer exposure times will produce degradation of the treated cellophane.

#### FUTURE WORK PLANNED

1. Quantative measurements of the amounts of light absorbed and transmitted by the cellophane sheets will be made, using a uranyl oxalate actinometer.
2. Degradation of cellulose will be determined by increase in cuprammonium fluidity as well as by loss in breaking strength.
3. End-group analyses of the degraded cellulose will be made to determine whether oxidative or hydrolytic degradation has occurred.
4. Degradative methods for materials other than cellulose will be explored.
5. ~~Degradation~~ accelerators other than ferric ion will be studied. Especial attention will be given to those which can be conveyed to the textile substrate in vapor form, rather than as a non volatile liquid or solid.

#### DETAILS

##### Materials

The cellophane sheet used was Avisco type 300 PI. This was originally received as 12 inch by 13 inch sheets, 0.00081 inch thick, plasticized with a water miscible glycol. For use in the current degradation studies, the plasticizer was removed by extraction with deionized water. The wet, swollen sheets were then clamped in wooden frames such that, on drying in air 70°F. and 65% R.H., they shrank to their original dimensions, giving smooth flat sheets. Wooden embroidery hoops, approximately 7 inches in diameter, were found to make excellent mounting frames. The machine direction of the cellophane was readily discerned from the faint striations, especially noticeable in the original, plasticized cellophane. This machine direction was marked on each sheet. For the measurements of breaking strength,

described below, 1 inch by 6 inch die-cut samples were used, with the 6 inch dimension parallel to the striations.

The "untreated" cellophane, with plasticizer removed, and dried at 70°F. 65% R.H. was found to weigh 3.25 mg per sq. cm. It was 20.6 microns thick. Oven dried (105°C.) untreated cellophane was found to weigh 2.57 mg. per sq. cm. There the untreated cellophane adsorbs 26.5% its weight of water at 70°F., 65% R.H.

Cellophane was "treated" with ferric nitrate as follows:

Untreated sheets were agitated gently for 15 minutes in a 0.1% solution of ferric nitrate in dilute nitric acid (pH3). The sheets were then rinsed several times in deionized water and excess surface liquid was blotted off. Wet pick ups were found to be approximately 145%. The sheets were mounted on wooden hoops to dry at 70°F., 65% R.H. The treated cellophane weighed 3.26 mg. per sq. cm.

The treated cellophane appeared to be evenly impregnated with ferric nitrate, as evidenced by its uniform pale yellow color. The uniformity of color was further checked by light transmission measurements.

The ferric ion content of treated cellophane was determined using a colorimetric method based on the red color of the ferric thiocyanate complex. Ferric ion was extracted from the treated cellophane with hydrochloric acid and, after adjusting to an HCl concentration of 0.5N, potassium thiocyanate was added and the intensity of the red color was determined spectrophotometrically at 4850 Å. The treated cellophane contained 0.09% ferric ion. This corresponds to 0.4% ferric nitrate, somewhat above the value of 0.15% expected on the basis of wet pick up of ferric nitrate solution, and indicates that the ferric ion is substantive to the cellophane.

The percent light transmittance through single sheets of untreated and treated cellophane was measured over the range of wave lengths from

3600 to 7000 A. At a wave length of 3600 A, the untreated transmitted 88% of the light, while the treated cellophane transmitted 70% of the light. At 4000 A the untreated transmitted 89%, and the treated transmitted 81%. At wave lengths from 5000 to 7000 A the treated and untreated sheets transmitted approximately 91% and 90%, respectively.

#### Apparatus and Experimental Procedure.

Separate arrays of treated and untreated cellophane were exposed to light in the following manner:

Three sheets of the cellophane were mounted in tandem in a frame such that distances from the light source were 41, 44, and 47 cm., respectively. The carbon arc of a Fadeometer was used as the light source. Corex windows were used to filter out light below 2750 A. A 1cm. thick layer of 0.04M cupric sulfate solution and a 0.5cm. thickness of glass were used to filter out essentially all light below 3600A and most of the light above 7000 A. The glass-cupric sulfate filter was placed 2cm. in front of the front cellophane sheet. A small aperture was used to give a beam of filtered light 1.5 cm. in diameter which passed through the sheets. The cellophane sheets were enclosed so that they received only the beam of filtered light. Since the sheets transmit only part of the light falling on them, the second sheet received less light than the first sheet, and the third sheet received still less light. A black surface was placed behind the third sheet to completely absorb the light transmitted through this sheet.

In this initial experiment, the arrays were given 5 hour exposures to the light. The exposed sheets were allowed to condition 48 hours at 70°F., 65% R.H. and then 1 x 6 inch strips were die cut (6 in. in the machine direction) so that the 1.76 sq. cm. exposed area was approximately in the center of the strip. The strips were tested for breaking strength and the breaking strengths compared to those of treated and untreated



unexposed samples. All of the strips had breaking strengths of 10.5 lbs, neither the ferric nitrate nor light exposure causing any measurable deterioration. Since in previous work under contract Cml-136 it has been shown that 0.01% ferric nitrate in cotton can catalyze photooxidative degradation, it is expected that as the current studies are extended to longer exposure times, the treated cellophane will be deteriorated.